

## SOME EFFECTS OF WATER-VAPOR ADSORPTION ON SODIUM CHLORIDES AT 25C<sup>1</sup>

By *Henry M. Papee*<sup>2</sup>

University of Ottawa

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### ABSTRACT

The surface of sodium-chloride microcrystals has been "strained" in an electrodeless high-frequency discharge. Surface areas of the blue product obtained in this way, after exposure to water vapor at 25C and unit relative vapor pressure, were plotted against time and the rates compared with the sintering rate of a normal surface. Induction periods were found in both cases indicating surface adsorption, during which time the surface does not change appreciably. The rates of sintering were found to differ considerably indicating that sintering of the "blue" surface is much slower than that of the "white" one. Both phenomena were found to follow first-order kinetics with respect to surface. The possible role of activated NaCl in ice nucleation and water coalescence in the atmosphere is discussed.

### 1. Introduction

Benson and collaborators [1] have measured the surface energy of sodium chloride and have found in some cases small effects due to impurities occluded in the product obtained in an electrostatic precipitator [2].

It has been suggested that lattice dislocations in crystals may promote initiation of solidification of slightly supercooled water vapor [3] and it was observed [4] that surfaces of lead di-iodide particles known for their property of nucleating ice crystals [5; 6; 7; 8] sinter rather slowly when exposed to water vapor. It was therefore decided to carry out a qualitative investigation with the object of synthesizing sodium-chloride particles with strained surface and of determining anomalies in sintering during exposure to water vapor, as compared with the data obtained for the sintering of pure 'normal' sodium chloride under the same conditions.

Colored varieties of NaCl exist in nature [9], the color being due to lattice defects [10; 11], and it is known that such defects can be induced in the lattice by various forms of radiochemical excitation.

### 2. Materials

Sodium chloride of large specific areas was used. The product was obtained from a C.P.-grade reagent by evaporation in a stream of dry nitrogen, free of oxygen, and precipitation in an electrostatic precipitator [12]. Care was taken to avoid conditions that might have led to generation of nitrate and sodium impurities [2].

Analysis of the product obtained indicated the absence of such contaminations.

### 3. Experimental

All manipulations of the reagent, related to the filling of the reaction cells were performed under an atmosphere of dry nitrogen, obtained by boiling liquid nitrogen at a steady rate, electrically, into a dry box for at least 6 hr. At that time, the relative humidity was usually below 1 per cent as checked with a hygrometer. A weighed reaction cell that could be fitted directly to the BET assembly was then filled with the salt and weighed again. The cell was then evacuated to less than  $10^{-4}$  mm of Hg, at a temperature of 120C. Heat was supplied by a calibrated heater that could be controlled to within a degree C; the heater was placed around the cell and the oxygen thermometer assembly of the BET apparatus. The heating process usually lasted 12 hr. Silicon grease was used for lubrication of the joints. Surface measurements by BET method were performed using nitrogen at relative pressure below 0.15 [13]. The samples were then exposed to water vapor, using the apparatus shown in fig. 1. Water vapor was supplied for this purpose from the reservoir A, which contained distilled and outgassed water. It was seen that small amounts of gases other than water vapor would considerably reduce the rate of sintering so that care had to be taken to preboil the water under vacuum before experimentation was initiated. To carry out a hydration of the sample, stopcock C leading to the BET main was closed and stopcock B opened. One second before the desired time, B was closed and C opened. Fast evaporation followed since the circuit was at all times under high vacuum, and the diffusion pump was backed by an evacuated 24-

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<sup>2</sup> Present affiliation: Division of Applied Chemistry, National Research Council, Ottawa, Canada.

liter flask in parallel with a fast mechanical pump. The whole operation was performed at 25C: this was the temperature to which the room was thermo-regulated. This temperature, and unit partial pressure of water vapor, were chosen because a microcalorimetric study of water adsorption on NaCl [14] was performed under these conditions. The sample was then pumped for 1 hr at 25C and thereafter for 3 hr under heating at 120C. A BET surface measurement was then carried out.

It was observed during preliminary experiments in electrodeless discharges that there was only a change in the "surface" of the powdered product that was exposed directly to the ionized atmosphere. Stirring the salt during the process therefore appeared necessary to ensure good yields, and a cell of the type represented in fig. 2 was used for the preparation of the blue product. The cell was supported on two brass shafts which were soldered on to a copper jacket 0.5 mm thick. The jackets were plated electrolytically directly on both ends of the tube and were 4 cm long. The reactor tube was 1.5 cm in internal diameter, 55 cm overall length, and of Pyrex glass. Grooved tubular blocks were soldered concentrically on both shafts about 3 cm from the tube itself, and thick copper wire was loosely looped in the groove. This wire was used to secure contact between the oscillator and the reactor while the latter was being rotated about its axis. One of the brass shafts was kept anchored in a glass-tube socket, while the other was elastically connected to an electric motor by means of a glass rod. Silicon grease was used on all joints. The tube was rotated at 50 rpm. A 1-kw, 23-Megahertz push-pull oscillator was used to excite the reactor and was operated at 150 w only, to prevent sintering of the salt by overheating. Quantities of about 2 g of the finely divided NaCl were introduced into the tube after outgassing the product under vacuum at 120C for 12 hr. The reactor was then evacuated and outgassed to  $5 \times 10^{-4}$  mm of mercury. It was then disconnected from the vacuum circuit and connected to the motor and the oscillator. The salt became faintly brown several seconds after the discharge was induced, this color changing quickly to a greyish blue which in turn changed with time to violet. Since it soon became apparent that the discharge was becoming fainter with time because of the chlorine evolved, the apparatus was pumped down twice at 2-hr intervals and once more after 12 hr. The salt had tendencies to stick to the wall of the discharge tube and was removed from there, to insure good mixing, by disconnecting the oscillator periodically and submitting the tube to the action of an electromagnetic vibrator for one minute. The whole operation usually lasted 70 hr. Small increases (of about 5 per cent) in specific surface areas were observed when working with particles of initial

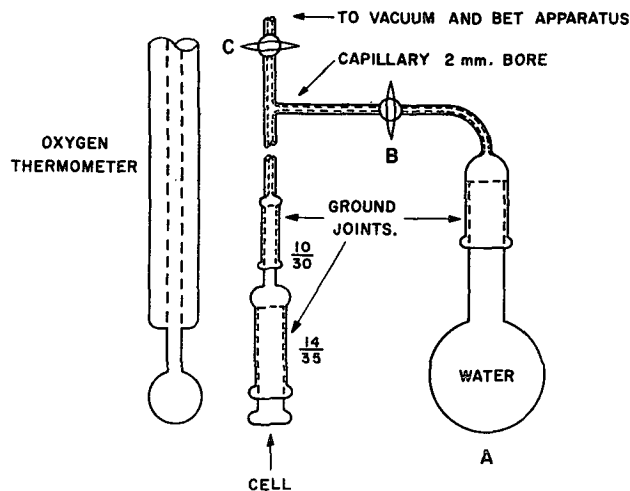


FIG. 1. Assembly for sintering of NaCl powders under water vapor (extension of BET apparatus).

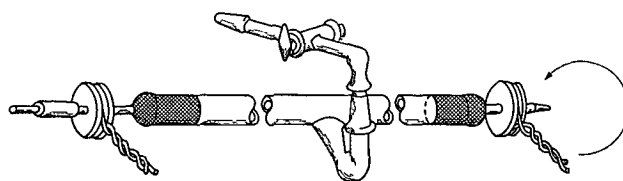


FIG. 2. Discharge-tube assembly for treatment of NaCl particles.

specific surface below  $10 \text{ m}^2$  per g. These particles tended to agglomerate less than the finer ones, whose specific area decreased slightly during treatment in the discharge.

Several batches of the product were prepared in this way from a batch of constant specific surface, and the salt showed a tendency to agglomerate in small lumps; the lot was ground finely in a mortar, sieved through a 100-Mesh screen and mixed thoroughly by shaking. The final product obtained in this way was then used for the experiments on sintering.

Preliminary experiments showed that a change in color of the salt, when exposed to radiation, will take place even when the product has previously been slightly hydrated. Water vapor at saturated water-vapor pressure was admitted for this purpose to the reactor for 100 sec and the tube then left for one hour. The blue coloration of the salt appeared in this case, in a manner similar to that of the other experiments and almost immediately after the discharge was induced.

Evolution of chlorine could be observed when the final product was dissolved in water; the resulting solution was alkaline.

Treatment of sodium chloride under the same conditions but in the presence of metallic sodium led to similar although faster changes, but a substantial decrease in the specific surface occurred in this case. There was no need to evacuate the reactor during this experiment.

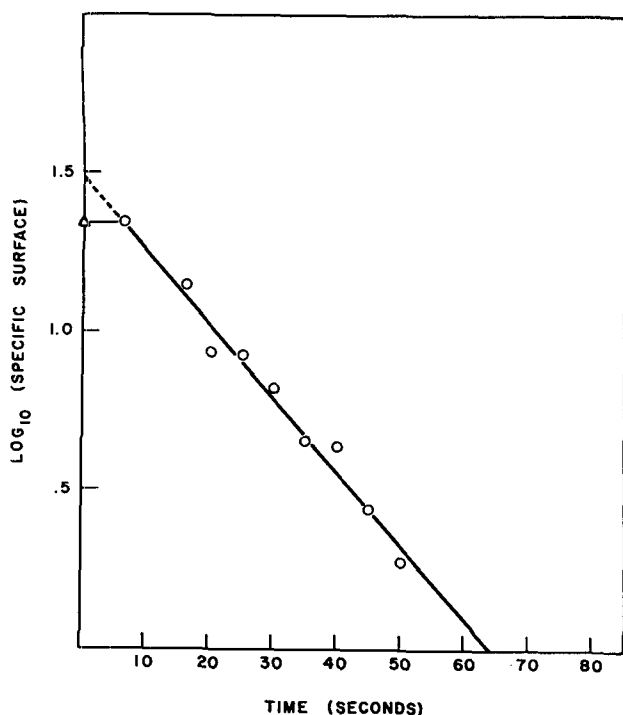


FIG. 3. Sintering of pure sodium chloride on exposure to water vapor: plot of the decimal logarithm of specific surface against time of exposure.

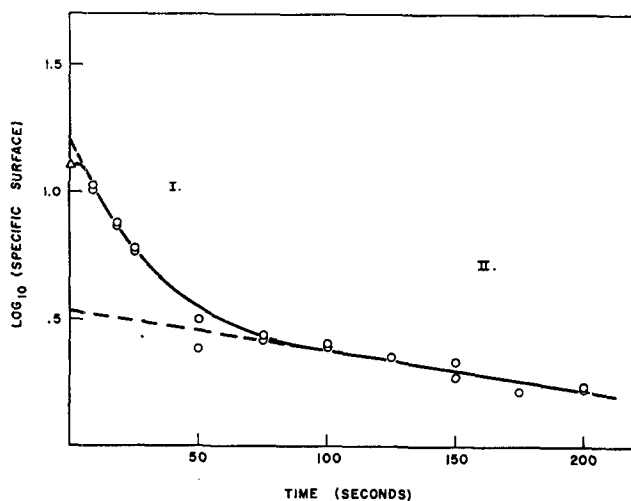


FIG. 4. Sintering of "strained" sodium chloride on exposure to water vapor: plot of the decimal logarithm of specific surface against time of exposure.

#### 4. Results

Fig. 3 shows the sintering process of "white" sodium-chloride particles of an initial surface area of 22.1 m<sup>2</sup> per g when exposed to water vapor. The initial surface area was determined from five separate samples, and then the average was taken. An inhibition period during which the surface remains essentially unchanged can be seen. The plot shows at the same time that the phenomenon follows first-order kinetics with respect

to surface. The parameters of the line are:

$$\begin{aligned} \text{Slope:} & \quad -0.023 \pm 0.001 \text{ sec}^{-1} \\ \text{Intercept:} & \quad 1.48 \pm 0.04. \end{aligned}$$

Every point of the plot was obtained by sintering a fresh quantity of salt of the same initial surface area.

Fig. 4 shows the process of sintering of sodium-chloride microcrystals of a "blue" surface. After hydration, each sample was pumped at 25C for 1 hr and a surface measurement was carried out. A heater was then placed around the sample and pumping was continued for 3 hr with the sample at 120C. This was followed by another surface determination by BET. Both results are recorded on the curve.

Due to the process of grinding and sieving, a substantial amount of the "white unstrained" surface was exposed, as confirmed by microscopic examination. Nevertheless the process of sintering follows a different pattern from the one represented in fig. 3. It can be seen that the somewhat complex exponential process, which sets in at the start, in fig. 4, becomes linear with time indicating a first order rate. Comparison with fig. 3 suggests that, within the limits of error, the second part of the curve of fig. 4 represents the sintering of the strained "blue" surface only, the white one being completely sintered already. Parameters of the slow process of sintering of the blue surface are thus computed and are:

$$\begin{aligned} \text{Slope:} & \quad -0.0016 \pm 0.0002 \text{ second}^{-1} \\ \text{Intercept:} & \quad 0.54 \pm 0.06. \end{aligned}$$

Assuming that the two processes of sintering take place simultaneously, the separate sintering of the "white" surface can be estimated here by extrapolating to zero time the linear portion II of the curve. Hence the "blue" surface corresponding to the first part of the curve can be calculated and the "white" surface estimated taking the difference. This procedure gives the results of fig. 5, the parameters of the line being the following:

$$\begin{aligned} \text{Slope:} & \quad -0.026 \pm 0.002 \text{ second}^{-1} \\ \text{Intercept:} & \quad 1.09 \pm 0.02. \end{aligned}$$

It can be seen that the slope obtained in this way agrees well with the value for the slope of the line on fig. 3.

#### 5. Discussion

The results indicate that there is a substantial difference between the rates of sintering of sodium chloride, depending on the nature of the surface. Sodium chloride which has surfaces strained by treatment in electric discharges sinters considerably more slowly than clean and unstrained salt. These results

appear significant when one remembers that sodium-chloride particles are present in the atmosphere [15; 16; 17] where processes leading to radiochemical excitation often take place. Furthermore, the coloration induced in the salt by the treatment previously described appears to be relatively stable, and although "blue" samples of about 20 m<sup>2</sup> per g lose their color relatively quickly when exposed to water vapor, crystals of surface below 10 m<sup>2</sup> per g remain blue even when the liquid phase appears in the container during hydration. These samples can be kept for weeks in the open without changing color appreciably despite what might be expected when dealing with samples containing colloidal sodium in the outer strata of the lattice. Furthermore, since it was shown recently [18] that rates of sintering of sodium chloride microcrystals depend strongly on the relative pressure of water vapor, it is thought that a sodium-chloride particle in the atmosphere will maintain a large specific surface for a long time after being activated by radiochemical excitation and will therefore maintain its properties as a nucleus for a long time. The case of lead di-iodide is somewhat similar, for its newly prepared (and therefore often distorted [19; 20]) photosensitive surfaces favour the formation of ice particles, although the mechanism of purely physical adsorption of water vapor on its surfaces (and the building of a large number of layers [21]) may be less effective for cloud seeding than in the case of activated NaCl particles. In fact, because there are differences in mobilities between elementary chlorine (found occluded in the "treated" crystals), sodium in the lattice of sodium chloride, and sodium and chloride ions and *F* centres in the salt [22], electrical gradients across a NaCl particle with a "blue" surface are possible. It is therefore conceivable that adsorption of water vapor on a particle of this kind which is initially electroneutral, will give rise to the production of electric charges on its surface, which in turn may favour an accumulation of water molecules around it (a sort of electrostriction [23]) and promote further growth of the particle or droplet [24; 25] at suitable conditions. Finally, after solution of an "activated" nucleus, a droplet resulting from the process, because of its NaOH content generated by the reaction of elementary sodium with water, will conceivably have a lower vapor pressure than a normal droplet of water or an NaCl solution under the same conditions, and will therefore grow more quickly until the growth reaches the size of mechanical precipitation.

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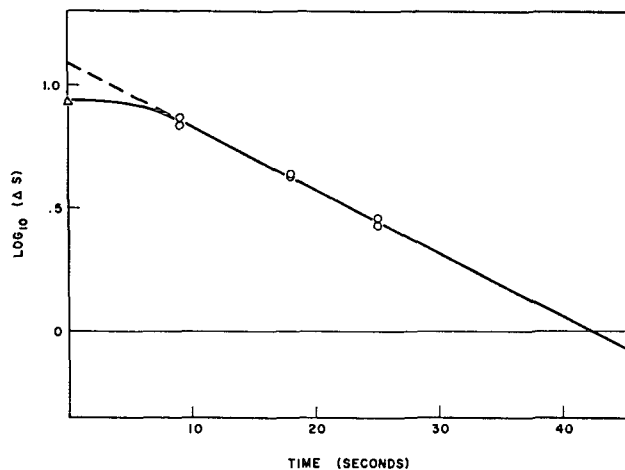


FIG. 5. Sintering of the unstrained surface of sodium chloride present in the "blue" salt, on exposure to water vapor: plot of the decimal logarithm of computed amount of salt against time of exposure.

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